# PATENT SPECIFICATION (11) 1 436 945

1 436 945

(21) Application No. 959/73 (22) Filed 8 Jan. 1973
(23) Complete Specification filed 8 Jan. 1974
(44) Complete Specification published 26 May 1976
(51) INT. CL.[2] C23C 9/04
(52) Index at acceptance
C7U 6 7C 7E 7L
C7F 1B2 2Z4 4E 4F 4K


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(19)


## (54) BORIDING COMPOSITIONS


(71) We, BORAX CONSOLIDATED LIMITED (a British Company) of Borax House, Carlisle Place, London SW1P 1HT, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—


This invention relates to boriding compositions i.e. compositions by means of which surfaces of articles may be treated to provide extremely hard-wearing boride layers. Articles that can be treated according to the invention may be fabricated from steels, nickel and/or cobalt alloys, tungsten carbide, metals of groups IVA, VA and VIA of the Periodic Table and alloys thereof. The compositions of the invention are particularly suitable for boriding tungsten carbide.

Hitherto, boriding of metals has been carried out by three main processes, gas boriding; salt bath boriding and boriding with solid boriding agents. In gas boriding there are two practical gaseous sources or boron viz. diborane and boron trichloride. These agents can be used to boride very small articles but they are difficult to handle because of the toxicity and flammability of diborane and the rapid hydrolysis of boron trichloride in air so in consequence neither agent is much used.

Salt boriding may be carried out with or without electrolysis. Borate based baths, whether electrolytic or not, suffer from the problem that a tough coating of borate forms on the borided article when cold which is very difficult to remove. Electrolytic baths based on alkali metal halides with fluoborate as a source or boron do not have this problem but they are only suitable for boriding simple objects, for example round bars.

The third process is boriding with solid boriding agents where the source of boron can be the element itself, a metal boride, boron carbide or ferroboron. All these types of solid boriding need the presence of an activator which may be borax, boric oxide and/or a halide. Boron is generally too expensive for this use and metal borides are not generally available so usually boron carbide or ferroboron is used.

When a steel or low alloy steel is borided by any of the above processes boron combines with iron to form either $Fe_2B$ or both $Fe_2B$ and FeB. Whether one or each phase is formed depends on the "boron potential" of the boriding medium. At high boron potentials both borides are formed with FeB on the outside and $Fe_2B$ between it and the substrate. At low boron potentials only $Fe_2B$ is formed. Although FeB is harder than $Fe_2B$ it suffers from the disadvantage of being more brittle. Ideally on a borided article, FeB should be absent or, if present, in as thin a layer as possible.

According to the present invention, boriding compositions are provided which can be used in a simple process to provide hard-wearing layers to the surface of articles. When the said articles are fabricated of a steel or low alloy steel the surface layer consists essentially of $Fe_2B$.

Specification No. 1,283,201 proposes a composition for the bonding of metals comprising in powder form a boriding agent and, as activator, from 1 to 10% by weight calculated on the total weight of boriding agent and activator of a fluoborate. Specification No. 1,384,169 proposes a process for boriding metals in a boriding powder consisting of a boron-yielding agent, at least one alkali metal, alkaline earth metal or ammonium halide as an activator, and free carbon and in particular a process wherein the free carbon content of the boriding powder is from 2 to 40% by weight.

The present invention provides a solid

pulverulent boriding composition comprising in admixture a boriding agent, an activator, as herein defined, and carbon or graphite; the carbon and graphite being present in an amount of from 50 to 90 weight per cent.

The boriding agent can be calcium hexaboride, boron carbide, amorphous boron and ferroboron or mixtures thereof.

The term "activator" as used herein means a compound which promotes rapid diffusion of boron into the surface of an article. The activator can be an alkali or alkaline earth metal fluoride or chloride, ammonium fluoride or chloride, a mixture of any of the aforementioned compounds with boric oxide, an alkali metal acid fluoride or an alkali or alkaline earth metal fluoborate.

The compositions of this invention are powders which contain, in addition to a boriding agent and an activator, carbon or graphite in an amount of from 50 to 90 weight per cent. It has been found that such a composition containing a high proportion of the diluent carbon or graphite, is at least of comparable effectiveness, weight for weight, as a similar composition having no carbon diluent, and the high-carbon composition is of course less expensive than the corresponding undiluted composition. It has also been found that the diluent carbon or graphite suppresses the formation of a cake of hard material on the borided article which is difficult to remove.

An example of a composition of the invention is 50-90 weight percent graphite 8 to 48 weight percent boriding agent and 2 to 20 weight per cent activator, with the proviso that the activator is present in an amount greater than 10 per cent of the boriding agent.

The compositions are illustrated by the following typical examples:—

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|---|---|---|
| 1. | Graphite | 75 parts by weight |
| | Boron carbide | 20 parts by weight |
| | Sodium fluoride | 4 parts by weight |
| | Boric oxide | 1 part by weight |
| 2. | Graphite | 70 parts by weight |
| | Boron carbide | 10 parts by weight |
| | Ferro-boron | 15 parts by weight |
| | Potassium fluoborate | 5 parts by weight |
| 3. | Graphite | 50 parts by weight |
| | Amorphous boron | 10 parts by weight |
| | Calcium hexaboride | 30 parts by weight |
| | Ammonium chloride | 10 parts by weight |

To boride an article one of the compositions described above is heated to a temperature of 700 to 1100°C in close contact with the article. The following example illustrates the procedure carried out for an article fabricated of mild steel.

The article was placed on a thin layer of a mixture containing 75 parts by weight graphite, 20 parts by weight boron carbide and 5 parts by weight sodium fluoborate in a suitable steel or ceramic container with a lid. More powder was added until the article was completely covered. The container was placed in a furnace and heated to 900°C and held at this temperature for 3 hours. The container was removed and the article was cleaned.

On examining a cross-section of the article an even layer 200 microns in thickness was observed on the substrate. Subsequently this was found to be $Fe_2B$.

A preferred composition for the boriding of tungsten carbide is

| | |
|---|---|
| Graphite | 50 parts by weight |
| Boron carbide | 45 parts by weight |
| Potassium fluoborate | 5 parts by weight. |

WHAT WE CLAIM IS:—

1. A solid pulverulent boriding composition comprising in admixture a boriding agent, an activator, as herein defined, and carbon or graphite being present in an amount of from 50 to 90 weight per cent.

2. A composition as claimed in claim 1, wherein the boriding agent is calcium hexaboride, boron carbide, amorphous boron or ferroboron or a mixture of any two or more thereof.

3. A composition as claimed in claim 1 or 2, wherein the activator is an alkali or alkaline earth metal fluoride or chloride, ammonium fluoride or chloride, a mixture of any of the aforementioned compounds with boric oxide, an alkali metal acid fluoride or an alkali or alkaline earth metal fluoborate.

4. A composition as claimed in claim 1, comprising in admixture 50 to 90 weight per cent graphite, 8 to 48 weight per cent boriding agent and 2 to 20 weight per cent activator, with the proviso that the activator is present in an amount greater than 10 per cent of the boriding agent.

5. A composition as claimed in claim 1 for use in boriding tungsten carbide comprising 50 parts by weight graphite, 45 parts by weight boron carbide and 5 parts by weight potassium fluorborate.

6. A composition as claimed in claim 1 substantially as described herein.

7. A process for the boriding of metallic articles which comprises heating the

article to a temperature of from 700 to 1100°C in contact with a composition as claimed in any of claims 1 to 6.

8. A process as claimed in claim 7 wherein the metal article to be treated is fabricated from steel, nickel and/or cobalt alloys, tungsten carbide, a metal of group IVA, VA or VIA of the Periodic Table or alloys thereof.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1976.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.